

09/508057

410 Rec'd PCT/PTO 07 MAR 2000

TRANSMITTAL LETTER TO THE UNITED STATES

ATTORNEY'S DOCKET NUMBER 0732/970223DESIGNATED/ELECTED OFFICE (DO/EO/US)  
CONCERNING A FILING UNDER 35 U.S.C. 371

U.S. APPLICATION NO. (If known, see 37 CFR 1.5)

INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/EP 98/05588	3 September 1998	11 September 1997

TITLE OF INVENTION: PROCESS FOR PREPARING METALLOCENES

APPLICANT(S) FOR DO/EO/US Carsten BINGEL, Berthold SCHIEMENZ, Markus GOERES

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. /X/ This is a FIRST submission of items concerning a filing under 35 U.S.C. 371.
  2. / / This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371.
  3. /X/ This express request to begin national examination procedures (35 U.S.C.371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
  4. /x / A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
  5. /X/ A copy of the International Application as filed (35 U.S.C. 371(c)(2)).
    - a./X/ is transmitted herewith (required only if not transmitted by the International Bureau).
    - b./ / has been transmitted by the International Bureau.
    - c./ / is not required, as the application was filed in the United States Receiving Office (RO/USO).
  6. /X/ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
  7. / / Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)).
    - a./ / are transmitted herewith (required only if not transmitted by the International Bureau).
    - b./ / have been transmitted by the International Bureau.
    - c./ / have not been made; however, the time limit for making such amendments has NOT expired.
    - d./ / have not been made and will not be made.
  8. / / A translation of the amendments to the claims under PCT Article 19(35 U.S.C. 371(c)(3)).
  9. /X/ An oath or declaration of the inventor(s)(35 U.S.C. 171(c)(4)).
  10. / / A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).
- Items 11. to 16. below concern other document(s) or information included:
- 11./X/ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
  - 12./X/ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
  13. / / A FIRST preliminary amendment.  
/ / A SECOND or SUBSEQUENT preliminary amendment.
  14. / / A substitute specification.
  15. / / A change of power of attorney and/or address letter.
  - 16./x / Other items or information.  
International Search Report  
International Preliminary Examination Report

U.S. Appln. No. (If Known) INTERNATIONAL APPLN. NO. ATTORNEY'S DOCKET NO.  
PCT/EP 98/05588 0732/970223

		CALCULATIONS	PTO USE ONLY
17. /X/ The following fees are submitted			
BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5)):			
Search Report has been prepared by the			
EPO or JPO.....	\$840.00	840.00	
International preliminary examination fee paid to USPTO			
(37 CFR 1.482).....	\$750.00		
No international preliminary examination fee paid to			
USPTO (37 CFR 1.482) but international search fee paid			
to USPTO (37 CFR 1.445(a)(2)).....\$700.00			
Neither international preliminary examination fee			
(37 CFR 1.482) nor international search fee			
(37 CFR 1.445(a)(2)) paid to USPTO .....\$ 970.00			
International preliminary examination fee paid to			
USPTO (37 CFR 1.482) and all claims satisfied pro			
-visions of PCT Article 33(2)-(4).....\$96.00			
ENTER APPROPRIATE BASIC FEE AMOUNT =		\$ 840.00	
Surcharge of \$130.00 for furnishing the oath or declaration			
later than / / 20 / /30 months from the earliest			
claimed priority date (37 CFR 1.492(e)).			
Claims	Number Filed	Number Extra	Rate
Total Claims	3 -20		X\$18.
Indep.Claims	1 -3		X\$78.
Multiple dependent claim(s)(if applicable)			+270.
TOTAL OF ABOVE CALCULATION		=	840.00
Reduction of 1/2 for filing by small entity, if applicable.			
Verified Small Entity statement must also be filed			
(Note 37 CFR 1.9, 1.27, 1.28).			
SUBTOTAL		=	840.00
Processing fee of \$130. for furnishing the English			
translation later than / /20 / /30 months from the			
earliest claimed priority date (37 CFR 1.492(f)). +			
TOTAL NATIONAL FEE		=	840.00
Fee for recording the enclosed assignment (37 CFR 1.21(h)).			
The assignment must be accompanied by an appropriate cover			
sheet (37 CFR 3.28, 3.31) \$40.00 per property = 40.00			
TOTAL FEES ENCLOSED		= \$	880.00
Amount to be			
refunded:		\$	
Charged		\$	

- a./X/ A check in the amount of \$ 880. to cover the above fees is enclosed.
- b./ / Please charge my Deposit Account No. \_\_\_\_\_ in the amount of \$ \_\_\_\_\_ to cover the above fees. A duplicate copy of this sheet is enclosed.
- c./X/ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 11-0345. A duplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:  
KEIL & WEINKAUF  
1101 Connecticut Ave., N.W.  
Washington, D. C. 20036

Herbert B. Keil  
NAME  
18,967  
Registration No.

SIGNATURE

0732/970223

- 1 -

## Description

## Process for preparing metallocenes

The present invention relates to a process for preparing metallocenes.

5           Metallocenes can be used, if desired in combination with one or more cocatalysts, as catalyst components for the polymerization and copolymerization of olefins. In particular, halogen-containing metallocenes are used as catalyst precursors which can, 10 for example, be converted by means of an aluminoxane into a polymerization-active cationic metallocene complex (EP-A-129368).

          Metallocenes are not only of great interest for the polymerization of olefins, but they can also be 15 used as hydrogenation, epoxidation, isomerization and C-C-coupling catalysts (Chem. Rev., 92 (1992), 965-994).

          The preparation of metallocenes is known per se (US 4,752,597; US 5,017,714; EP-A-320762; EP-A-416815; 20 EP-A-537686; EP-A-669340; H.H. Britzinger et al., Angew. Chem., 107 (1995), 1255; H.H. Britzinger et al., J. Organomet. Chem. 232 (1982), 233). For this purpose, for example, cyclopentadienyl-metal compounds can be reacted with halides of transition metals such as 25 titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum, cerium, thorium or uranium. It is also known from the literature that metallocenes can be obtained, for example, by reaction of cyclopentadienes with amides of group IV of the 30 Periodic Table of the Elements (US 5,597,935; R.F. Jordan et al., Organometallics, 15 (1996), 4030).

          It is an object of the invention to find a process for preparing metallocenes which has wide applicability and, for example, is also suitable for 35 preparing highly substituted, bulky metallocenes.

It has now surprisingly been found that this object is achieved by use of specific adducts of the formula (I).

The invention accordingly provides a process  
5 for preparing a metallocene, which comprises reacting a ligand starting compound with an adduct of the formula (I),



where  $M^1$  is a metal of group III, IV, V or VI of the  
10 Periodic Table of the Elements or an element of the lanthanide or actinide series, preferably titanium, zirconium or hafnium, particularly preferably zirconium,

X are identical or different and are each halogen,  $C_1$ -  
15  $C_{10}$ -alkoxy,  $C_6$ - $C_{10}$ -aryloxy,  $C_1$ - $C_{10}$ -alkylsulfonate such as mesylate, triflate, nonaflate,  $C_6$ - $C_{10}$ -arylsulfonate such as tosylate, benzenesulfonate,  $C_1$ - $C_{10}$ -alkylcarboxylate such as acetate, formate, oxalate or 1,3-dicarbonylate such as acetylacetonate or fluorinated 1,3-  
20 dicarbonylate, in particular chlorine, bromine, particularly preferably chlorine,

n is an integer and is 2,3,4,5 or 6 and corresponds to the oxidation number of the metal  $M^1$ ,

a is an integer or fraction and  $0 < a \leq 4$  and a is  
25 preferably in the range from 0.5 to 2.5 and is in particular 1, 1.5 or 2,

and D is a linear, cyclic or branched oligoether or polyether containing at least two oxygen atoms or an oligothioether or polythioether containing at least two  
30 sulfur atoms, for example dimethoxymethane, diethoxymethane, 1,2-dimethoxyethane, 1,2-diethoxyethane, 1,1,2,2-tetramethoxyethane, pentaerythritol tetramethyl ether, sorbitol hexamethyl ether, diethylene glycol dimethyl ether, diethylene glycol  
35 diethyl ether, 1,2,3-propanetriol trimethyl ether, 1,2,3-propanetriol triethyl ether, triethylene glycol

dimethyl ether, tetraethylene glycol dimethyl ether, pentaethylene glycol dimethyl ether, polyethylene glycol dimethyl ether, 1,3-propanediol dimethyl ether, 1,2-dimethoxycyclohexane, 1,2-dimethoxybenzene, a crown  
5 ether such as 18-crown-6, dibenzo-18-crown-6, 15-crown-5, 12-crown-4, dimethyl thioglycol, trimethyl thioglycerol, thia-18-crown-6, di(methyl)ethylene thioglycol, in particular 1,2-dimethoxyethane.

Illustrated examples of adducts of the formula  
10 (I), which do not, however, restrict the scope of the invention, are:

ZrCl<sub>4</sub>(1,2-dimethoxyethane)  
ZrCl<sub>4</sub>(dimethyl thioglycol)  
ZrCl<sub>4</sub>(1,2-diethoxyethane)  
15 ZrCl<sub>4</sub>(1,3-dimethoxypropane)  
ZrCl<sub>4</sub>(1,3-di(methylthio)propane)  
ZrCl<sub>4</sub>(18-crown-6)  
ZrCl<sub>4</sub>(dibenzo-18-crown-6)  
ZrCl<sub>4</sub>(1,2-dimethoxycyclohexane)  
20 ZrCl<sub>4</sub>(1,2-methoxybenzene)  
ZrCl<sub>4</sub>(diethylene glycol dimethyl ether)  
ZrCl<sub>4</sub>(1,2,3-propanetriol triethyl ether)  
ZrCl<sub>4</sub>(trimethyl thioglycerol)  
ZrCl<sub>4</sub>(triethylene glycol dimethyl ether)  
25 ZrCl<sub>4</sub>(tetraethylene glycol dimethyl ether)  
ZrCl<sub>4</sub>(O-isopropyl)<sub>2</sub>(1,2-dimethoxyethane)  
ZrCl<sub>4</sub>(O-ethyl)<sub>2</sub>(1,2-dimethoxyethane)  
ZrCl<sub>4</sub>(pentaerythritol tetramethyl ether)  
ZrBr<sub>4</sub>(1,2-dimethoxyethane)  
30 ZrBr<sub>4</sub>(diethylene glycol dimethyl ether)  
ZrBr<sub>4</sub>(1,2,3-propanetriol triethyl ether)  
ZrBr<sub>4</sub>(triethylene glycol dimethyl ether)  
ZrBr<sub>4</sub>(tetraethylene glycol dimethyl ether)  
Zr(O-isopropyl)<sub>4</sub>(1,2-dimethoxyethane)  
35 Zr(O-phenyl)<sub>4</sub>(1,2-dimethoxyethane)  
Zr(OEt)<sub>4</sub>(diethylene glycol dimethyl ether)

- Zr(O-tert-butyl)<sub>4</sub>(1,2,3-propanetriol triethyl ether)  
Zr(O-isopropyl)<sub>4</sub>(triethylene glycol dimethyl ether)  
Zr(OMe)<sub>4</sub>(tetraethylene glycol dimethyl ether)  
Zr(OMe)<sub>4</sub>(1,2-dimethoxyethane)
- 5 TiCl<sub>4</sub>(1,2-dimethoxyethane)  
TiCl<sub>4</sub>(dimethyl thioglycol)  
TiCl<sub>4</sub>(1,3-dimethoxypropane)  
TiCl<sub>3</sub>(1,2-dimethoxyethane)<sub>1.5</sub>  
TiCl<sub>3</sub>(dimethyl thioglycol)<sub>1.5</sub>
- 10 TiCl<sub>4</sub>(18-crown-6)  
TiCl<sub>3</sub>(18-crown-6)  
TiCl<sub>3</sub>(18-crown-6)<sub>1.5</sub>  
TiCl<sub>4</sub>(dibenzo-18-crown-6)  
TiCl<sub>4</sub>(diethylene glycol dimethyl ether)
- 15 TiCl<sub>3</sub>(diethylene glycol dimethyl ether)<sub>1.5</sub>  
TiCl<sub>4</sub>(sorbitol hexamethyl ether)  
TiCl<sub>3</sub>(sorbitol hexamethyl ether)<sub>1.5</sub>  
Ti(O-isopropyl)<sub>4</sub>(1,2-dimethoxyethane)  
HfCl<sub>4</sub>(1,2-dimethoxyethane)
- 20 HfCl<sub>4</sub>(dimethyl thioglycol)  
HfBr<sub>4</sub>(1,2-dimethoxyethane)  
HfCl<sub>4</sub>(18-crown-6)  
HfBr<sub>4</sub>(18-crown-6)  
Hf(O-isopropyl)<sub>4</sub>(1,2-dimethoxyethane)
- 25 HfCl<sub>4</sub>(diethylene glycol dimethyl ether)  
HfCl<sub>4</sub>(1,2,3-propanetriol triethyl ether)  
HfCl<sub>4</sub>(triethylene glycol dimethyl ether)  
HfCl<sub>4</sub>(tetraethylene glycol dimethyl ether)  
HfCl<sub>4</sub>(diethylene glycol diethyl ether)
- 30 CrCl<sub>3</sub>(1,2-dimethoxyethane)  
CrCl<sub>3</sub>(18-crown-6)  
MoCl<sub>3</sub>(1,2-dimethoxyethane)  
MoCl<sub>4</sub>(1,2-dimethoxyethane)  
MoCl<sub>4</sub>(dibenzo-18-crown-6)
- 35 VCl<sub>3</sub>(1,2-dimethoxyethane)  
VCl<sub>4</sub>(1,2-dimethoxyethane)

- Vl<sub>3</sub>(1,2-dimethoxyethane)  
VF<sub>4</sub>(1,2-dimethoxyethane)  
NbCl<sub>4</sub>(1,2-dimethoxyethane)  
NbCl<sub>4</sub>(18-crown-6)  
5 TaCl<sub>4</sub>(1,2-dimethoxyethane)  
TaCl<sub>4</sub>(18-crown-6)  
CeCl<sub>3</sub>(1,2-dimethoxyethane)  
NdCl<sub>3</sub>(1,2-dimethoxyethane)  
ThCl<sub>4</sub>(1,2-dimethoxyethane)  
10 UCl<sub>4</sub>(1,2-dimethoxyethane)

Adducts of the formula (I) can be prepared from transition metal compounds of the formula (Ia),

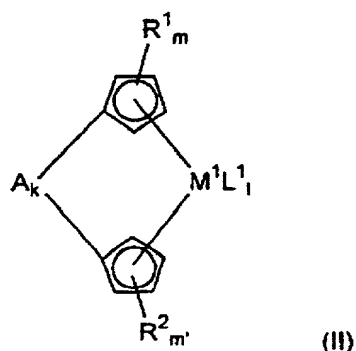


- 15 where M<sup>1</sup>, X and n have the same meanings as in formula (I), by reaction with an oligoether or polyether or an oligothioether or polythioether D in an inert solvent. D is a linear, cyclic or branched oligoether or  
20 polyether containing at least two oxygen atoms or an oligothioether or polythioether, containing at least two sulfur atoms, for example dimethoxymethane, diethoxymethane, 1,2-dimethoxyethane, 1,2-diethoxyethane, 1,1,2,2-tetramethoxyethane, pentaerythritol  
25 tetramethyl ether, sorbitol hexamethyl ether, diethylene glycol dimethyl ether, diethylene glycol diethyl ether, 1,2,3-propanetriol trimethyl ether, 1,2,3-propanetriol triethyl ether, triethylene glycol dimethyl ether, tetraethylene glycol dimethyl ether,  
30 pentaethylene glycol dimethyl ether, polyethylene glycol dimethyl ether, 1,3-propanediol dimethyl ether, 1,2-dimethoxycyclohexane, 1,2-dimethoxybenzene, a crown ether such as 18-crown-6, dibenzo-18-crown-6, 15-crown-5, 12-crown-4, dimethyl thioglycol, trimethyl  
35 thioglycerol, thia-18-crown-6, di(methylthio)ethylene, in particular 1,2-dimethoxyethane.

The adducts of the formula (I) can be synthesized separately and isolated or can be generated during the process of the invention for preparing the metallocene. The molar ratio of metal  $M^1$  to  
 5 oligoether/polyether or oligothioether/polythioether in this reaction is generally from 100 to 0.01, preferably from 10 to 0.5.

The process of the invention can be used to prepare various types of metallocene, for example  
 10 bridged or unbridged biscyclopentadienyl complexes as are described, for example, in EP 128 368, EP 561 479, EP 545 304 and EP 576 970, monocyclopentadienyl complexes such as bridged amidocyclopentadienyl complexes as are described, for example, in EP 416 815,  
 15 multinuclear cyclopentadienyl complexes as described in EP 632 063,  $\pi$ -ligand-substituted tetrahydropentalenes as described in EP 659 758 or  $\pi$ -ligand-substituted tetrahydroindenes as described in EP-661 300.

Preference is given to preparing metallocenes  
 20 of the formula (II),



where  $M^1$  is a transition metal of group III, IV, V or VI of the Periodic Table of the Elements or a lanthanide  
 25 or actinide metal, preferably zirconium, hafnium, titanium,

$L^1$  are identical or different and are each a halogen atom, preferably chlorine, a  $C_1$ - $C_{20}$ -group such as a  $C_1$ -



C<sub>20</sub>-alkoxy group or a C<sub>1</sub>-C<sub>20</sub>-aryloxy group, or L<sup>1</sup> can together form a ring system with M<sup>1</sup>,

l is an integer from 1 to 4, preferably 2 or 3, in particular 2,

- 5 R<sup>1</sup> and R<sup>2</sup> are identical or different and are each, independently of one another, a hydrogen atom, halogen, a C<sub>1</sub>-C<sub>40</sub>-group such as C<sub>1</sub>-C<sub>20</sub>-alkyl, in particular a methyl group, ethyl group, propyl, isopropyl, butyl, sec-butyl, tert-butyl, cyclohexyl, C<sub>6</sub>-C<sub>24</sub>-aryl which may  
 10 in turn be substituted, in particular a phenyl or naphthyl group, C<sub>2</sub>-C<sub>24</sub>-heteroaryl such as pyridyl, furyl, thienyl, pyrimidyl, quinolyl, C<sub>1</sub>-C<sub>10</sub>-alkoxy, C<sub>2</sub>-C<sub>10</sub>-alkenyl, C<sub>7</sub>-C<sub>20</sub>-arylalkyl, C<sub>7</sub>-C<sub>20</sub>-alkylaryl, C<sub>6</sub>-C<sub>18</sub>-aryloxy, C<sub>1</sub>-C<sub>10</sub>-haloalkyl, C<sub>6</sub>-C<sub>10</sub>-haloaryl, C<sub>2</sub>-C<sub>10</sub>-alkynyl, C<sub>3</sub>-C<sub>20</sub>-alkylsilyl, such as trimethylsilyl, triethylsilyl, tert-butyldimethylsilyl, triisopropylsilyl, C<sub>3</sub>-C<sub>20</sub>-arylsilyl such as triphenylsilyl, or C<sub>3</sub>-C<sub>20</sub>-alkylarylsilyl such as dimethylphenylsilyl, diphenylmethylsilyl or diphenyl-tert-butylsilyl and R<sup>1</sup>  
 20 and R<sup>2</sup> in each case together with the atoms of the cyclopentadienyl ring which connect them may form a monocyclic or polycyclic C<sub>3</sub>-C<sub>25</sub> ring system, in particular an indenyl, fluorenyl, benzindenyl or acenaphthindenyl system, which may in turn be  
 25 substituted, and R<sup>1</sup> and R<sup>2</sup> in each case together with A may form a ring system,

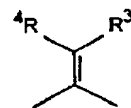
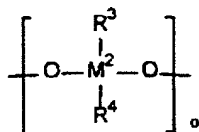
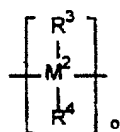
m is 5 when k = 0 and m is 4 when k = 1,

m' is 5 when k = 0 and m' is 4 when k = 1,

k is 0 or 1, with the metallocene being unbridged when

- 30 k = 0 and bridged when k = 1,

A is a bridge such as



or  $=BR^3$ ,  $AIR^3$ ,  $-S-$ ,  $-SO-$ ,  $-SO_2-$ ,  $=NR^3$ ,  $=PR^3$ ,  $=P(O)R^3$ , o-phenylene, 2,2'-bisphenylene,

where  $M^2$  is carbon, silicon, germanium, tin, nitrogen or phosphorus, preferably carbon, silicon or germanium, in particular carbon or silicon, and A together with one or more radicals  $R^1$  and/or  $R^2$  may form a monocyclic or polycyclic ring system,

o is 1, 2, 3 or 4, preferably 1 or 2,

$R^3$  and  $R^4$  are identical or different and are each, independently of one another, a hydrogen atom, halogen, a  $C_1$ - $C_{20}$ -group such as  $C_1$ - $C_{20}$ -alkyl, in particular a methyl group,  $C_6$ - $C_{14}$ -aryl, in particular a phenyl or naphthyl group,  $C_1$ - $C_{10}$ -alkoxy,  $C_2$ - $C_{10}$ -alkenyl,  $C_7$ - $C_{20}$ -arylalkyl,  $C_7$ - $C_{20}$ -alkylaryl,  $C_6$ - $C_{10}$ -aryloxy,  $C_1$ - $C_{10}$ -fluoroalkyl,  $C_6$ - $C_{10}$ -haloaryl,  $C_2$ - $C_{10}$ -alkynyl,  $C_3$ - $C_{20}$ -alkylsilyl, such as trimethylsilyl, triethylsilyl, tert-butyldimethylsilyl,  $C_3$ - $C_{20}$ -arylsilyl, such as triphenylsilyl, or  $C_3$ - $C_{20}$ -alkylarylsilyl such as dimethylphenylsilyl, diphenylsilyl or diphenyl-tert-butylsilyl and  $R^3$  and  $R^4$  may form a monocyclic or polycyclic ring system.

Illustrated examples of metallocenes, which do not, however, restrict the scope of the invention, are:

dimethylsilanediylbis(indenyl)zirconium dichloride  
 dimethylsilanediylbis(2-methylindenyl)zirconium dichloride  
 dimethylsilanediylbis(2,4,6-trimethylindenyl)zirconium dichloride  
 dimethylsilanediylbis(2,5,6-trimethylindenyl)zirconium dichloride  
 dimethylsilanediylbis[1-(2-methyl-4-phenylindenyl)]zirconium dichloride  
 dimethylsilanediylbis[1-(2-methylindenyl)]zirconium dichloride

- dimethylsilanediylbis[1-(2-methyl-4-(1-naphthyl)indenyl)]zirconium dichloride
- dimethylsilanediylbis[1-(2-methyl-4-(2-naphthyl)indenyl)]zirconium dichloride
- 5 dimethylsilanediylbis[1-(2-methyl-4-mesitylindenyl)]zirconium dichloride
- dimethylsilanediylbis[1-(2-methyl-4-(2-methylphenyl)indenyl)]zirconium dichloride
- dimethylsilanediylbis[1-(2-methyl-4-(2,3-
- 10 dimethylphenyl)indenyl)]zirconium dichloride
- dimethylsilanediylbis[1-(2-methyl-4-(2,5-dimethylphenyl)indenyl)]zirconium dichloride
- dimethylsilanediylbis[1-(2-methyl-4-(2,6-dimethylphenyl)indenyl)]zirconium dichloride
- 15 dimethylsilanediylbis[1-(2-methyl-4-(2,3-diethylphenyl)indenyl)]zirconium dichloride
- dimethylsilanediylbis[1-(2-methyl-4-(3,5-dimethylphenyl)indenyl)]zirconium dichloride
- dimethylsilanediylbis[1-(2-methyl-4-(2-
- 20 biphenyl)indenyl)]zirconium dichloride
- dimethylsilanediylbis[1-(2-methyl-4-(4-diphenyl)indenyl)]zirconium dichloride
- dimethylsilanediylbis[1-(2-methyl-4-(3,5-biphenylphenyl)indenyl)]zirconium dichloride
- 25 dimethylsilanediylbis[1-(2-methyl-4-(3,5-diisopropylphenyl)indenyl)]zirconium dichloride
- dimethylsilanediylbis[1-(2-methyl-4-(2,4,6-trimethoxyphenyl)indenyl)]zirconium dichloride
- dimethylsilanediylbis[1-(2-methyl-4-(4-N,N-
- 30 dimethylaminophenyl)indenyl)]zirconium dichloride
- dimethylsilanediylbis[1-(2-methyl-4-(3-N,N-dimethylaminophenyl)indenyl)]zirconium dichloride
- dimethylsilanediylbis[1-(2-methyl-4-(2-N,N-dimethylaminophenyl)indenyl)]zirconium dichloride
- 35 dimethylsilanediylbis[1-(2-methyl-4-(4-trifluoromethylphenyl)indenyl)]zirconium dichloride

- dimethylsilanediylbis[1-(2-methyl-4-(3-trifluoromethylphenyl)indenyl)]zirconium dichloride
- dimethylsilanediylbis[1-(2-methyl-4-(2-trifluoromethylphenyl)indenyl)]zirconium dichloride
- 5 dimethylsilanediylbis[1-(2-methyl-4-(3,5-bis-(trifluoromethyl)phenyl)indenyl)]zirconium dichloride
- dimethylsilanediylbis[1-(2-methyl-4-(2,4-bis(trifluoromethyl)phenyl)indenyl)]zirconium dichloride
- 10 dimethylsilanediylbis[1-(2-methyl-4,5-benzoindenyl)]zirconium dichloride
- dimethylsilanediylbis[1-(2-methyl- $\alpha$ -acenaphthindenyl)]zirconium dichloride
- dimethylsilanediylbis[1-(2-methyl-4,6-diisopropylindenyl)]zirconium dichloride
- 15 dimethylsilanediylbis[1-(2-ethyl-4-phenylindenyl)]zirconium dichloride
- dimethylsilanediylbis[1-(2-ethyl-4-naphthylindenyl)]zirconium dichloride
- 20 dimethylsilanediylbis[1-(2-isopropyl-4-(phenylindenyl)]zirconium dichloride
- dimethylsilanediylbis[1-(2-isopropyl-4-(1-naphthyl)indenyl)]zirconium dichloride
- dimethylsilanediylbis[1-(2-isopropyl-4-(2-naphthyl)indenyl)]zirconium dichloride
- 25 dimethylsilanediylbis[1-(2-isopropyl-4-(4-methylphenyl)indenyl)]zirconium dichloride
- dimethylsilanediylbis[1-(2-isopropyl-4-(3,5-dimethylphenyl)indenyl)]zirconium dichloride
- 30 dimethylsilanediylbis[1-(2-isopropyl-4-(4-trifluoromethylphenyl)indenyl)]zirconium dichloride
- dimethylsilanediylbis[1-(2-isopropyl-4-(3,5-bis(trifluoromethyl)phenyl)indenyl)]zirconium dichloride
- 35 dimethylsilanediylbis[1-(2-isopropyl-4-(4-methoxyphenyl)indenyl)]zirconium dichloride

- dimethylsilanediylbis[1-(2-isopropyl-4-(2-furyl)indenyl)]zirconium dichloride
- dimethylsilanediylbis[1-(2-cyclohexyl-4-(1-naphthyl)indenyl)]zirconium dichloride
- 5 dimethylsilanediylbis[1-(2-cyclohexyl-4-phenylindenyl)]zirconium dichloride
- dimethylsilanediylbis[1-(2,4-diphenylindenyl)]zirconium dichloride
- dimethylsilanediylbis[1-(2,4-dicyclohexylindenyl)]zirconium dichloride
- 10 dimethylsilanediylbis[1-(2-methyl-4-phenylindenyl)]hafnium dichloride
- dimethylsilanediylbis[1-(2-methyl-4-(1-naphthyl)indenyl)]hafnium dichloride
- 15 dimethylsilanediylbis[1-(2-ethyl-4-(naphthyl)indenyl)]hafnium dichloride
- dimethylsilanediylbis[1-(2-methyl-4-mesitylindenyl)]hafnium dichloride
- dimethylsilanediylbis[1-(2-methyl-4-(2-methylphenyl)indenyl)]hafnium dichloride
- 20 dimethylsilanediylbis[1-(2-methyl-4-(2,3-dimethylphenyl)indenyl)]hafnium dichloride
- dimethylsilanediylbis[1-(2-cyclohexyl-4-phenylindenyl)]hafnium dichloride
- 25 dimethylsilanediylbis(2,3,5-trimethylcyclopentadienyl)zirconium dichloride
- dimethylsilanediylbis(2-methyl-4-tert-butylcyclopentadienyl)zirconium dichloride
- dimethylsilanediylbis(fluorenyl)zirconium dichloride
- 30 methylphenylsilanediylbis[1-(2-methyl-4-phenylindenyl)]zirconium dichloride
- methylphenylsilanediylbis[1-(2-methyl-4-naphthylindenyl)]zirconium dichloride
- methylphenylsilanediylbis[1-(2-methyl-4-(2,3-dimethylphenyl)indenyl)]zirconium dichloride
- 35 diphenylsilanediylbis(1-indenyl)zirconium dichloride

- diphenylsilanediylbis[1-(2-methylindenyl)]zirconium  
dichloride
- diphenylsilanediylbis[1-(2-methyl-4-  
phenylindenyl)]zirconium dichloride
- 5 diphenylsilanediylbis[1-(2-methyl-4-  
naphthylindenyl)]zirconium dichloride
- diphenylsilanediylbis[1-(2-methyl-4-(2,3-  
dimethylphenyl)indenyl)]zirconium dichloride
- 10 1,2-ethanediylbis[1-(2-methyl-4-  
phenylindenyl)]zirconium dichloride
- 1,2-ethanediylbis[1-(2-methyl-4-(1-  
naphthyl)indenyl)]zirconium dichloride
- 1,2-ethanediylbis[1-(2-methyl-4-(2,3-  
dimethylphenyl)indenyl)]zirconium dichloride
- 15 1,2-ethanediylbis[1-(2-cyclohexyl-4-phenylindenyl)]  
zirconium dichloride
- 1,2-ethanediylbis[1-(2-methyl-4-3,5-  
bis(trifluoromethyl)phenylindenyl)]zirconium dichloride
- 1,2-ethanediylbis(fluorenyl)zirconium dichloride
- 20 1,2-ethanediylbis(2,3,5-  
trimethylcyclopentadienyl)zirconium dichloride
- 1,2-ethanediylbis(2-methyl-4-tert-  
butylcyclopentadienyl)zirconium dichloride
- 1,2-ethanediylbis[1-(2-methyl-4-phenylindenyl)]titanium
- 25 dichloride
- 1,2-ethanediylbis[1-(2-methyl-4-(1-  
naphthyl)indenyl)]titanium dichloride
- 1,2-ethanediylbis(indenyl)]titanium dichloride
- 1,2-ethanediylbis(tetrahydroindenyl)]titanium
- 30 dichloride
- 1,2-butanediylbis[1-(2-methyl-4-  
phenylindenyl)]zirconium dichloride
- 1,2-butanediylbis[1-(2-methyl-4-(1-naphthyl)indenyl)]  
zirconium dichloride
- 35 1,2-butanediylbis[1-(2-methyl-4-(2-  
naphthyl)indenyl)]zirconium dichloride

- 1,2-butanediylbis[1-(2-methyl-4-(3,5-bis(trifluoromethyl)phenylindenyl)]zirconium dichloride  
isopropylidenebis[1-(2-methyl-4-phenylindenyl)]zirconium dichloride
- 5 isopropylidenebis[1-(2-methyl-4-(2,3-dimethylphenylindenyl)]dimethylzirconium  
isopropylidenebis[1-(2-methyl-4-(1-naphthyl)indenyl)]zirconium dichloride  
isopropylidenebis[1-(2-cyclohexyl-4-phenyl)indenyl)]zirconium dichloride
- 10 isopropylidenebis[1-(2-methyl-4-(3,5-bis(trifluoromethyl)phenylindenyl)]zirconium dichloride  
isopropylidenebis(fluorenyl)zirconium dichloride  
isopropylidene(indenyl)(fluorenyl)zirconium dichloride
- 15 isopropylidene(cyclopentadienyl)(fluorenyl)zirconium  
dichloride  
isopropylidene(cyclopentadienyl)(indenyl)zirconium  
dichloride  
isopropylidenebis(2-methyl-4-tert-butylcyclopentadienyl)zirconium dichloride
- 20 bis(cyclopentadienyl)zirconium dichloride  
bis(n-butylcyclopentadienyl)zirconium dichloride  
bis(1,3-dimethylcyclopentadienyl)zirconium dichloride  
bis(pentamethylcyclopentadienyl)zirconium dichloride
- 25 bis(indenyl)zirconium dichloride  
bis(fluorenyl)zirconium dichloride  
bis[2-methyl-4-phenylindenyl]zirconium dichloride  
bis[2-methyl-4-(2,3-dimethylphenyl)indenyl]zirconium  
dichloride
- 30 bis[2-methyl-4-(1-naphthyl)indenyl]zirconium dichloride  
bis[2-methyl-4-mesitylindenyl]zirconium dichloride  
bis[2-ethyl-4-(3,5-bis(trifluoromethyl)phenylindenyl)]zirconium dichloride  
bis[2-cyclohexyl-4-phenylindenyl]zirconium dichloride
- 35 [4-( $\eta^5$ -cyclopentadienyl)-4,6,6-trimethyl( $\eta^5$ -4,5,6,7-tetrahydropentalenyl)]zirconium dichloride

[4-( $\eta^5$ -3'-trimethylsilylcyclopentadienyl)-4,6,6-trimethyl( $\eta^5$ -4,5,6,7-tetrahydropentalenyl)]zirconium dichloride

5 [4-( $\eta^5$ -3'-isopropylcyclopentadienyl)-4,6,6-trimethyl( $\eta^5$ -4,5,6,7-tetrahydropentalenyl)]zirconium dichloride

[4-( $\eta^5$ -fluorenyl)4-methyl-6-phenyl( $\eta^5$ -4,5,6,7-tetrahydropentalenyl)]zirconium dichloride

[4-( $\eta^5$ -indenyl)-4-methyl-6-phenyl( $\eta^5$ -4,5,6,7-tetrahydropentalenyl)]zirconium dichloride

10 [4-( $\eta^5$ -cyclopentadienyl)-4,7,7-trimethyl( $\eta^5$ -4,5,6,7-tetrahydroindenyl)]zirconium dichloride

[4-( $\eta^5$ -cyclopentadienyl)-4,7,7-trimethyl( $\eta^5$ -4,5,6,7-tetrahydroindenyl)]hafnium dichloride

15 [4-( $\eta^5$ -cyclopentadienyl)-4,7,7-trimethyl( $\eta^5$ -4,5,6,7-tetrahydroindenyl)]titanium dichloride

[4-( $\eta^5$ -3'-tert-butylcyclopentadienyl)-4,7,7-trimethyl( $\eta^5$ -4,5,6,7-tetrahydroindenyl)]zirconium dichloride

20 [4-( $\eta^5$ -3-isopropylcyclopentadienyl)-4,7,7-trimethyl( $\eta^5$ -4,5,6,7-tetrahydroindenyl)]zirconium dichloride

[4-( $\eta^5$ -3'-trimethylsilylcyclopentadienyl)-4,7,7-trimethyl( $\eta^5$ -4,5,6,7-tetrahydroindenyl)]zirconium dichloride

25 [4-( $\eta^5$ -3'-methylcyclopentadienyl)-4,7,7-trimethyl( $\eta^5$ -4,5,6,7-tetrahydroindenyl)]zirconium dichloride

[4-( $\eta^5$ -3'-methylcyclopentadienyl)-4,7,7-trimethyl( $\eta^5$ -4,5,6,7-tetrahydroindenyl)]zirconium dichloride  
dimethylsilanediyl(tert-butylamido)(tetramethyl- $\eta^5$ -cyclopentadienyl)titanium dichloride

30 1,2-ethanediyl(tert-butylamido)(tetramethyl- $\eta^5$ -cyclopentadienyl)titanium dichloride

dimethylsilanediyl(methylamido)(tetramethyl- $\eta^5$ -cyclopentadienyl)titanium dichloride



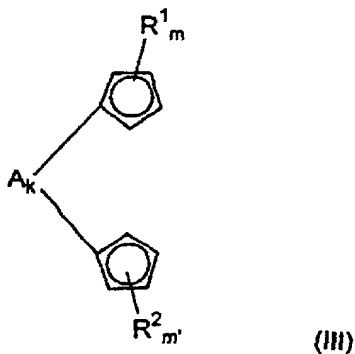
1,2-ethanediyl(methylamido)(tetramethyl- $\eta^5$ -  
cyclopentadienyl)titanium dichloride

dimethylsilanediyl(tert-butylamido)(2,4-dimethyl-2,4-  
pentadienyl)titanium dichloride

- 5 tetrachloro-[1-(bis( $\eta^5$ -1H-inden-1-ylidene)methylsilyl-3-  
 $\eta^5$ -cyclopenta-2,4-dien-1-ylidene-3- $\eta^5$ -9H-fluoren-9-  
ylidene-)butane]dizirconium.

To prepare metallocenes by the process of the  
invention, use is made of ligand starting compounds  
10 such as cyclopentadiene compounds, for example  
cyclopentadiene, indene or fluorene derivatives. These  
can be deprotonated by means of bases and the  
corresponding anions bind as ligands to transition  
metals to form metallocenes.

- 15 As ligand starting compounds for preparing  
metallocenes by the process of the invention,  
preference is given to using compounds of the formula  
(III),



- 20 where A, k,  $R^1$ ,  $R^2$ , m and  $m'$  have the same meanings as  
in formula (II).

- Illustrative examples of compounds of the  
formula (III), which do not, however, restrict the  
25 scope of the invention, are:

dimethylbis(indenyl)silane

dimethylbis(2-methylindenyl)silane

dimethylbis(2,4,6-trimethylindenyl)silane

- dimethylbis(2,5,6-trimethylindenyl)silane  
dimethylbis[1-(2-methyl-4-phenylindenyl)]silane  
dimethylbis[1-(2-methylindenyl)]silane  
dimethylbis[1-(2-methyl-4-(1-naphthyl)indenyl)]silane  
5 dimethylbis[1-(2-methyl-4-(2-naphthyl)indenyl)]silane  
dimethylbis[1-(2-methyl-4-mesitylindenyl)]silane  
dimethylbis[1-(2-methyl-4-(2-methylphenyl)indenyl)]silane  
dimethylbis[1-(2-methyl-4-(2,3-dimethylphenyl)indenyl)]silane  
10 dimethylbis[1-(2-methyl-4-(2,5-dimethylphenyl)indenyl)]silane  
dimethylbis[1-(2-methyl-4-(2,6-dimethylphenyl)indenyl)]silane  
15 dimethylbis[1-(2-methyl-4-(2,3-diethylphenyl)indenyl)]silane  
dimethylbis[1-(2-methyl-4-(3,5-dimethylphenyl)indenyl)]silane  
dimethylbis[1-(2-methyl-4-(2-biphenyl)indenyl)]silane  
20 dimethylbis[1-(2-methyl-4-(4-biphenyl)indenyl)]silane  
dimethylbis[1-(2-methyl-4-(3,5-diphenylphenyl)indenyl)]silane  
dimethylbis[1-(2-methyl-4-(3,5-diisopropylphenyl)indenyl)]silane  
25 dimethylbis[1-(2-methyl-4-(2,4,6-trimethoxyphenyl)indenyl)]silane  
dimethylbis[1-(2-methyl-4-(4-N,N-dimethylaminophenyl)indenyl)]silane  
dimethylbis[1-(2-methyl-4-(3-N,N-dimethylaminophenyl)indenyl)]silane  
30 dimethylbis[1-(2-methyl-4-(2-N,N-dimethylaminophenyl)indenyl)]silane  
dimethylbis[1-(2-methyl-4-(4-trifluoromethylphenyl)indenyl)]silane  
35 dimethylbis[1-(2-methyl-4-(3-trifluoromethylphenyl)indenyl)]silane

- dimethylbis[1-(2-methyl-4-(2-trifluoromethylphenyl)indenyl)]silane  
dimethylbis[1-(2-methyl-4-(3,5-bis(trifluoromethyl)phenyl)indenyl)]silane  
5 dimethylbis[1-(2-methyl-4-(2,4-bis(trifluoromethyl)phenyl)indenyl)]silane  
dimethylbis[1-(2-methyl-4,5-benzoindenyl)]silane  
dimethylbis[1-(2-methyl- $\alpha$ -acenaphthindenyl)]silane  
dimethylbis[1-(2-methyl-4,6-diisopropylindenyl)]silane  
10 dimethylbis[1-(2-ethyl-4-phenylindenyl)]silane  
dimethylbis[1-(2-ethyl-4-naphthylindenyl)]silane  
dimethylbis[1-(2-isopropyl-4-phenylindenyl)]silane  
dimethylbis[1-(2-isopropyl-4-(1-naphthyl)indenyl)]silane  
15 dimethylbis[1-(2-isopropyl-4-(2-naphthyl)indenyl)]silane  
dimethylbis[1-(2-isopropyl-4-(4-methylphenyl)indenyl)]silane  
dimethylbis[1-(2-isopropyl-4-(3,5-dimethylphenyl)indenyl)]silane  
20 dimethylbis[1-(2-isopropyl-4-(4-trifluoromethylphenyl)indenyl)]silane  
dimethylbis[1-(2-isopropyl-4-(3,5-bis(trifluoromethyl)phenyl)indenyl)]silane  
25 dimethylbis[1-(2-isopropyl-4-(4-methoxyphenyl)indenyl)]silane  
dimethylbis[1-(2-isopropyl-4-(2-furyl)indenyl)]silane  
dimethylbis[1-(2-cyclohexyl-4-(1-naphthyl)indenyl)]silane  
30 dimethylbis[1-(2-cyclohexyl-4-phenylindenyl)]silane  
dimethylbis[1-(2,4-diphenylindenyl)]silane  
dimethylbis[1-(2,4-dicyclohexylindenyl)]silane  
dimethylbis[1-(2,3,5-trimethylcyclopentadienyl)]silane  
dimethylbis[1-(2-methyl-4-tert-butylcyclopentadienyl)]silane  
35 dimethylbis(fluorenyl)]silane

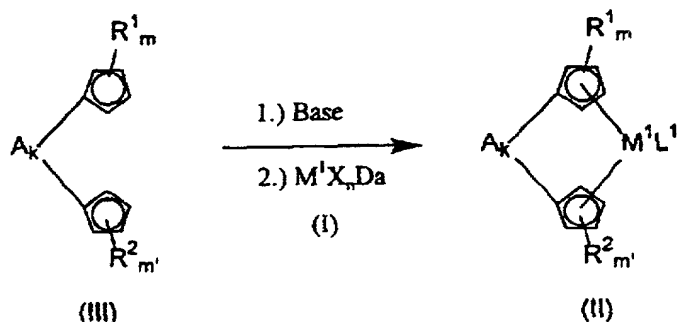
- methylphenylbis[1-(2-methyl-4-phenylindenyl)]silane  
methylphenylbis[1-(2-methyl-4-naphthylindenyl)]silane  
methylphenylbis[1-(2-methyl-4-(2,3-  
dimethylphenyl)indenyl)]silane
- 5 diphenylbis(1-indenyl)silane  
diphenylbis[1-(2-methylindenyl)]silane  
diphenylbis[1-(2-methyl-4-phenylindenyl)]silane  
diphenylbis[1-(2-methyl-4-naphthylindenyl)]silane  
diphenylbis[1-(2-methyl-4-(2,3-  
dimethylphenyl)indenyl)]silane
- 10 1,2-bis[1-(2-methyl-4-phenylindenyl)]ethane  
1,2-bis[1-(2-methyl-4-(1-naphthyl)indenyl)]ethane  
1,2-bis[1-(2-methyl-4-(2,3-  
dimethylphenyl)indenyl)]ethane
- 15 1,2-bis[1-(2-cyclohexyl-4-phenylindenyl)]ethane  
1,2-bis[1-(2-methyl-4-(3,5-  
bis(trifluoromethyl)phenylindenyl)]ethane  
1,2-bis(fluorenyl)ethane  
1,2-bis(2,3,5-trimethylcyclopentadienyl)ethane
- 20 1,2-bis(2-methyl-4-tert-butylcyclopentadienyl)ethane  
1,2-bis[1-(2-methyl-4-phenylindenyl)]butane  
1,2-bis[1-(2-methyl-4-(1-naphthyl)indenyl)]butane  
1,2-bis[1-(2-methyl-4-(2-naphthyl)indenyl)]butane  
1,2-bis[1-(2-methyl-4-(3,5-  
bis(trifluoromethyl)phenylindenyl)]butane
- 25 2,2-bis[1-(2-methyl-4-phenylindenyl)]propane  
2,2-bis[1-(2-methyl-4-(2,3-  
dimethylphenylindenyl)]dimethylzirconium
- 30 2,2-bis[1-(2-methyl-4-(1-naphthyl)indenyl)]propane  
2,2-bis[1-(2-cyclohexyl-4-phenyl)indenyl)]propane  
2,2-bis[1-(2-methyl-4-(3,5-  
bis(trifluoromethyl)phenylindenyl)]propane  
2,2-bis(fluorenyl)propane
- 35 2-(indenyl)-2-(fluorenyl)propane  
2-(cyclopentadienyl)-2-(fluorenyl)propane

- 2- (cyclopentadienyl) -2- (indenyl) propane  
[4- (cyclopentadienyl) -4,6,6-trimethyl ( $\eta^5$ -4,5,6,7-tetrahydropentalene)]  
[4- (3'-trimethylsilylcyclopentadienyl) -4,6,6-trimethyl-  
5 ( $\eta^5$ -4,5,6,7-tetrahydropentalene)  
[4- (3'-isopropylcyclopentadienyl) -4,6,6-trimethyl ( $\eta^5$ -4,5,6,7-tetrahydropentalene)  
[4- (fluorenyl) -4-methyl-6-phenyl ( $\eta^5$ -4,5,6,7-tetrahydropentalene)]  
10 [4- (indenyl) -4-methyl-6-phenyl ( $\eta^5$ -4,5,6,7-tetrahydropentalene)]  
[4- (cyclopentadienyl) -4,7,7-trimethyl ( $\eta^5$ -4,5,6,7-tetrahydroindene)]  
[4- (3'-tert-butylcyclopentadienyl) -4,7,7-trimethyl- ( $\eta^5$ -  
15 4,5,6,7-tetrahydroindene)]  
[4- (3-isopropylcyclopentadienyl) -4,7,7-trimethyl ( $\eta^5$ -4,5,6,7-tetrahydroindene)]  
[4- (3'-trimethylsilylcyclopentadienyl) -4,7,7-trimethyl ( $\eta^5$ -4,5,6,7-tetrahydroindene)]  
20 [4- (3'-methylcyclopentadienyl) -4,7,7-trimethyl ( $\eta^5$ -4,5,6,7-tetrahydroindene)]  
[4- (3'-methylcyclopentadienyl) -2,4,7,7-tetramethyl ( $\eta^5$ -4,5,6,7-tetrahydroindene)]  
dimethyl (tert-butylamido) (tetramethyl- $\eta^5$ -  
25 cyclopentadienyl) silane  
1- (tert-butylamido) -2- (tetramethyl- $\eta^5$ -cyclopentadienyl) ethane  
dimethyl (methylamido) (tetramethyl- $\eta^5$ -cyclopentadienyl) silane  
30 1- (methylamido) -2- (tetramethyl- $\eta^5$ -cyclopentadienyl) ethane  
dimethyl (tert-butylamido) - (2,4-dimethyl-2,4-pentadienyl) silane

[1-(bis(1H-inden-1-ylidene)methylsilyl)-3- $\eta^5$ -cyclopenta-2,4-dien-1-ylidene)-3- $\eta^5$ -9H-fluoren-9-ylidene)butane]

The preparation of metallocenes by the process of the invention is preferably carried out by  
 5 deprotonation of suitable ligand starting compounds, for example compounds of the formula (III), using bases in an inert solvent or solvent mixture and subsequent reaction with an adduct of the formula (I) which can be prepared separately and used as an isolated compound or  
 10 alternatively can be generated in situ during the process of the invention.

Preference is given to preparing metallocenes of the formula (II) from ligand starting compounds of the formula (III), as is illustrated in a  
 15 nonrestrictive way in the following reaction scheme,



where A, k,  $R^1$ ,  $R^2$ , m,  $m'$ ,  $M^1$ , X, n, D, a,  $L^1$  and I are defined as in formulae (I) and (II).

Nonrestrictive examples of suitable bases are  
 20 organolithium compounds such as n-butyllithium, sec-butyllithium, tert-butyllithium, methyllithium, organomagnesium compounds such as dibutylmagnesium, butyloctylmagnesium, Grignard compounds, alkali metal such as sodium, potassium, alkali metal hydrides such  
 25 as lithium hydride, sodium hydride, potassium hydride or alkali metal amides such as lithium amide, sodium amide, potassium amide, sodium hexamethyl disilazide, potassium hexamethyldisilazide, lithium

hexamethyldisilazide, lithium diisopropylamide, lithium diethylamide.

Suitable inert solvents are aliphatic or aromatic hydrocarbons such as toluene, xylene, benzene, mesitylene, pentane, hexane, heptane, cyclohexane, halogenated hydrocarbons such as 1,2-dichloroethane, o-dichlorobenzene, trichloroethylene, dichloromethane, ethers such as diethyl ether, dibutyl ether, methyl tert-butyl ether, anisole, THF, dioxane, 1,2-dimethoxyethane (DME), diglyme and also any mixtures of these.

The process of the invention is generally carried out in a temperature range from  $-120^{\circ}\text{C}$  to  $+300^{\circ}\text{C}$ , preferably in a temperature range from  $-78^{\circ}\text{C}$  to  $+150^{\circ}\text{C}$ , particularly preferably at a temperature in the range from  $0^{\circ}\text{C}$  to  $120^{\circ}\text{C}$ .

The molar ratio of the above-described suitable bases to ligand starting compounds, for example compounds of the formula (III), is generally in the range from 10 to 0.1, preferably from 4 to 0.5, particularly preferably from 3 to 0.8, in the process of the invention.

The molar ratio of adducts of the formula (I) to ligand starting compounds, for example compounds of the formula (III), is generally in the range from 100 to 0.01, preferably from 10 to 0.1, in the process of the invention.

The concentration of the ligand starting compounds in the reaction mixture is generally in the range from 0.0001 mol/l to 8 mol/l, preferably in the range from 0.01 mol/l to 3 mol/l, particularly preferably in the range from 0.1 mol/l to 2 mol/l.

The adducts of the formula (I) can be formed under the reaction conditions and reacted further without isolation. Preference is given to preparing the

adducts of the formula (I) separately and using them as isolated compounds in the process of the invention.

The reaction time is generally in the range from 5 minutes to 1 week, preferably in the range from 5 15 minutes to 48 hours.

The metallocenes which can be prepared by the process of the invention are highly active catalyst components for olefin polymerization. Depending on the substitution pattern of the ligands, the metallocenes 10 can be obtained as a mixture of isomers. For the polymerization, the metallocenes are preferably used in isomerically pure form. The use of the racemate is in most cases sufficient.

However, it is also possible to use the pure 15 enantiomer in the (+) or (-) form. Use of the pure enantiomers enables an optically active polymer to be prepared. However, the configurational isomers of the metallocenes should be separated, since the polymerization-active center (the metal atom) in these 20 compounds usually produces a polymer having different properties. For certain applications, for example soft moldings, this can be thoroughly desirable.

The metallocenes obtained in the process of the invention, in particular metallocenes of the formula 25 (II), are suitable for preparing a polyolefin by polymerization of at least one olefin in the presence of a catalyst comprising at least one cocatalyst and at least one metallocene. For the purposes of the present invention, the term polymerization encompasses both 30 homopolymerization and copolymerization.

The metallocenes prepared in the process of the invention, in particular metallocenes of the formula (II), can be used for the polymerization of one or more olefins of the formula  $R^{\alpha}\text{-CH=CH-R}^{\beta}$ , where  $R^{\alpha}$  and  $R^{\beta}$  are 35 identical or different and are each a hydrogen atom or a hydrocarbon radical having from 1 to 20 carbon atoms,



in particular from 1 to 10 carbon atoms, and  $R^{\alpha}$  and  $R^{\beta}$  together with the atoms connecting them can form one or more rings. Examples of such olefins are 1-olefins having from 2 to 40, preferably 2-10, carbon atoms, e.g. ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene or 1-octene, styrene, dienes such as 1,3-butadiene, isoprene, 1,4-hexadiene or cyclic olefins such as norbornene or ethylidenenorbornene.

Preference is given to homopolymerizing ethylene or propylene or copolymerizing ethylene with one or more cyclic olefins such as norbornene and/or one or more acyclic 1-olefins having from 3 to 20 carbon atoms, e.g. propylene and/or one or more dienes having from 4 to 20 carbon atoms, e.g. 1,3-butadiene or 1,4-hexadiene. Examples of such copolymers are ethylene-norbornene copolymers, ethylene-propylene copolymers and ethylene-propylene-1,4-hexadiene copolymers.

The polymerization is preferably carried out at a temperature of from -60 to 250°C, particularly preferably from 50 to 200°C. The pressure is preferably from 0.5 to 2000 bar, particularly preferably from 5 to 64 bar.

The polymerization can be carried out in solution, in bulk, in suspension or in the gas phase, continuously or batchwise, in one or more stages. A preferred embodiment is gas-phase and solution polymerization.

The catalyst used preferably comprises one metallocene compound. It is also possible to use two or more metallocene compounds, e.g. to prepare polyolefins having a broad or multimodal molar mass distribution.

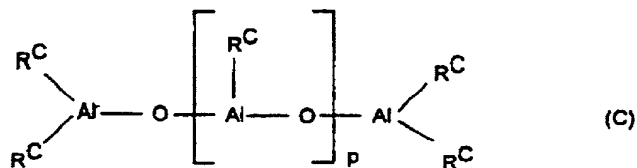
In principle, suitable cocatalysts are all compounds which, owing to their Lewis acidity, can convert the uncharged metallocene into a cation and

stabilize the latter ("labile coordination"). Furthermore, the catalyst or the anion formed therefrom should undergo no further reactions with the metallocenium cation (EP 427 697). The cocatalyst used  
 5 is preferably an aluminum compound and/or a boron compound.

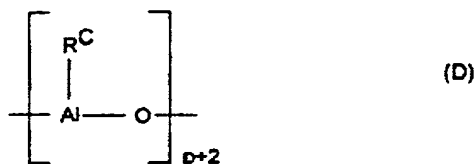
The boron compound preferably has the formula  $R^a_xNH_{4-x}BR^b_x$ ,  $R^a_xPH_{4-x}BR^b_4$ ,  $R^a_3CBR^b_4$  or  $BR^b_3$ , where x is from 1 to 4, preferably 3, the radicals  $R^a$  are identical or  
 10 different, preferably identical, and are  $C_1$ - $C_{10}$ -alkyl or  $C_6$ - $C_{18}$ -aryl or two radicals  $R^a$  together with the atoms connecting them form a ring and the radicals  $R^b$  are identical or different, preferably identical, and are  $C_6$ - $C_{18}$ -aryl which may be substituted by alkyl, haloalkyl  
 15 or fluorine. In particular,  $R^a$  is ethyl, propyl, butyl or phenyl and  $R^b$  is phenyl, pentafluorophenyl, 3,5-bis(trifluoromethyl)phenyl, mesityl, xylyl or tolyl (EP 277 003, EP 277 004 and EP 426 638).

The cocatalyst used is preferably an aluminum  
 20 compound such as aluminoxane and/or an aluminum alkyl.

The cocatalyst used is particularly preferably an aluminoxane, in particular of the formula C for the linear type and/or the formula D for the cyclic type,



25



where, in the formulae C and D, the radicals  $R^C$  are identical or different and are each hydrogen or a  $C_1$ -  
 30  $C_{20}$ -hydrocarbon group such as a  $C_1$ - $C_{18}$ -alkyl group, a  $C_6$ -

C<sub>18</sub>-aryl group or benzyl and p is an integer from 2 to 50, preferably from 10 to 35.

The radicals R<sup>c</sup> are preferably identical and are hydrogen, methyl, isobutyl, phenyl or benzyl, particularly preferably methyl. If the radicals R<sup>c</sup> are different, they are preferably methyl and hydrogen or alternatively methyl and isobutyl, with hydrogen or isobutyl preferably being present in a numerical proportion of from 0.01 to 40% (of the radicals R<sup>c</sup>).

The methods of preparing the aluminoxanes are known. The precise spatial structure of the aluminoxanes is not known (J. Am. Chem. Soc. (1993) 155, 4971). For example, it is conceivable that chains and rings are connected to form larger two-dimensional or three-dimensional structures.

Regardless of the method of preparation, all aluminoxane solutions have in common a variable content of unreacted aluminum starting compound which is present in free form or as adduct.

Before use in the polymerization reaction, it is possible to preactivate the metallocene compound using a cocatalyst, in particular an aluminoxane. This significantly increases the polymerization activity. The preactivation of the metallocene compound is preferably carried out in solution. Here, the metallocene compound is preferably dissolved in a solution of the aluminoxane in an inert hydrocarbon. Suitable inert hydrocarbons are aliphatic or aromatic hydrocarbons. Preference is given to using toluene.

The concentration of the aluminoxane in the solution is in the range from about 1% by weight to the saturation limit, preferably from 5 to 30% by weight, in each case based on the total amount of solution. The metallocene can be used in the same concentration, but it is preferably used in an amount of from 10<sup>-4</sup> to 1 mol per mol of aluminoxane. The preactivation time is from

5 minutes to 60 hours, preferably from 5 to 60 minutes. The preactivation is preferably carried out at a temperature of from  $-78^{\circ}$  to  $100^{\circ}\text{C}$ , preferably from  $10^{\circ}$  to  $80^{\circ}\text{C}$ .

5           The metallocene compound is preferably employed in a concentration, based on the transition metal, of from  $10^{-3}$  to  $10^{-8}$  mol, preferably from  $10^{-4}$  to  $10^{-7}$  mol, of transition metal per  $\text{dm}^3$  of solvent or per  $\text{dm}^3$  of reactor volume. The aluminoxane is preferably used in a  
10 concentration of from  $10^{-6}$  to  $10^{-1}$  mol, preferably from  $10^{-5}$  to  $10^{-2}$  mol, per  $\text{dm}^3$  of solvent or per  $\text{dm}^3$  of reactor volume. The other cocatalysts mentioned are used in approximately equimolar amounts to the metallocene compound. However, higher concentrations  
15 are also possible in principle.

          The aluminoxane can be prepared in various ways by known methods. One of the methods is, for example, to react an aluminum hydrocarbon compound and/or a hydride aluminum hydrocarbon compound with water  
20 (gaseous, solid, liquid or bound - for example as water of crystallization) in an inert solvent (for example toluene). An aluminoxane having different radicals  $\text{R}^{\text{C}}$  is prepared, for example, by reacting two different trialkylaluminums corresponding to the desired  
25 composition with water.

          To remove catalyst poisons present in the olefin, purification using an aluminum compound, preferably an aluminum alkyl such as trimethylaluminum or triethylaluminum, is advantageous. This purification  
30 can be carried out either in the polymerization system itself or the olefin is brought into contact with the aluminum compound and subsequently separated off again before being introduced into the polymerization system.

          As molar mass regulator and/or to increase the  
35 catalyst activity, hydrogen can be added in the process

of the invention. This enables low molecular weight polyolefins such as waxes to be obtained.

The metallocene compound is preferably reacted with the cocatalyst outside the polymerization reactor in a separate step using a suitable solvent. Application to a support can be carried out during this step.

In the process for preparing a polyolefin, a prepolymerization can be carried out with the aid of the metallocene compound. The prepolymerization is preferably carried out using the (or one of the) olefin(s) used in the polymerization.

The catalyst used can be supported. Application to a support enables, for example, the particle morphology of the polyolefin prepared to be controlled. Here, the metallocene compound can be reacted first with the support and subsequently with the cocatalyst. It is also possible to apply the cocatalyst to a support first and subsequently react it with the metallocene compound. Another possibility is to apply the reaction product of metallocene compound and cocatalyst to a support. Suitable support materials are, for example, silica gels, aluminum oxides, solid aluminoxane or other inorganic support materials such as magnesium chloride. Another suitable support materials is a polyolefin powder in finely divided form. The preparation of the supported cocatalyst can be carried out, for example, as described in EP 567 952.

Preferably, the cocatalyst, e.g. aluminoxane, is applied to a support such as silica gel, aluminum oxide, solid aluminoxane, another inorganic support material or a polyolefin powder in finely divided form and then reacted with the metallocene.

As inorganic supports, it is possible to use oxides which have been produced flame-pyrolytically by

combustion of element halides in a hydrogen/oxygen flame or can be prepared as silica gels in particular particle size distributions and particle shapes.

The preparation of the supported cocatalyst can  
5 be carried out, for example, as described in EP 578 838  
in the following manner in a stainless steel reactor of  
explosion-protected design having a pumped circulation  
system rated at 60 bar, with inert gas supply,  
temperature control by means of jacket cooling and a  
10 second cooling circuit via a heat exchanger in the  
pumped circulation system. The pumped circulation  
system draws in the reactor contents via a connection  
in the bottom of the reactor by means of a pump and  
pushes it into a mixer and through a riser line via a  
15 heat exchanger back into the reactor. The mixer is  
configured so that the inlet has a constricted pipe  
cross section in which an increased flow velocity  
results and into whose turbulence zone there is  
inserted, axially and counter to the flow direction, a  
20 thin feed line through which, pulsed, a defined amount  
of water can be fed in under 40 bar of argon. The  
reaction is monitored via a sampler on the pumped  
circuit.

However, other reactors are also suitable in  
25 principle.

The above-described reactor having a volume of  
16 dm<sup>3</sup> is charged with 5 dm<sup>3</sup> of decane under inert  
conditions. 0.5 dm<sup>3</sup> (= 5.2 mol) of trimethylaluminum are  
added at 25°C. 250 g of silica gel SD 3216-30 (Grace  
30 AG) which have been dried beforehand at 120°C in an  
argon-fluidized bed are then introduced into the  
reactor via a solids funnel and homogeneously  
distributed by means of the stirrer and the pumped  
circulation system. A total amount of 76.5 g of water  
35 is introduced into the reactor in portions of 0.1 cm<sup>3</sup>  
every 15 seconds over a period of 3.25 hours. The

pressure, which is due to argon and the gases evolved, is kept constant at 10 bar by means of a pressure regulating valve. After all the water has been introduced, the pumped circulation system is switched  
5 off and stirring is continued for another 5 hours at 25°C.

The supported catalyst prepared in this way is used as a 10% suspension in n-decane. The aluminum content is 1.06 mmol of Al per cm<sup>3</sup> of suspension. The  
10 isolated solid contains 31% by weight of aluminum and the suspension medium contains 0.1% by weight of aluminum.

Further possible ways of preparing a supported cocatalyst are described in EP 578 838.

15 The metallocene prepared according to the invention is then applied to the supported cocatalyst by stirring the dissolved metallocene with the supported cocatalyst. The solvent is removed and replaced by a hydrocarbon in which both cocatalyst and  
20 metallocene are insoluble.

The reaction to form the supported catalyst system is carried out at a temperature of from -20 to +120°C, preferably from 0 to 100°C, particularly preferably from 15 to 40°C. The metallocene is reacted  
25 with the supported cocatalyst by combining a 1-40% by weight suspension, preferably a 5-20% by weight suspension, of the cocatalyst in an aliphatic, inert suspension medium such as n-decane, hexane, heptane or diesel oil with a solution of the metallocene in an  
30 inert solvent such as toluene, hexane, heptane or dichloromethane or with the finely milled solid metallocene. Conversely, a solution of the metallocene can also be reacted with the solid cocatalyst.

The reaction is carried out by intensive  
35 mixing, for example by stirring, at a molar Al/M<sup>1</sup> ratio of from 100/1 to 10,000/1, preferably from 100/1 to

3000/1, and a reaction time of from 5 to 120 minutes, preferably from 10 to 60 minutes, particularly preferably from 10 to 30 minutes, under inert conditions.

5           During the reaction time for preparing the supported catalyst system, particularly when using metallocenes according to the invention having absorption maxima in the visible region, changes in the color of the reaction mixture occur and enable the  
10           progress of the reaction to be followed.

          After the reaction time has elapsed, the supernatant solution is separated off, for example by filtration or decantation. The solid which remains is washed from 1 to 5 times with an inert suspension  
15           medium such as toluene, n-decane, hexane, diesel oil or dichloromethane to remove soluble constituents in the catalyst formed, in particular to remove unreacted and therefore soluble metallocene.

          The supported catalyst system prepared in this  
20           way can be resuspended as a vacuum-dried powder or while still moist with solvent and be metered as suspension in one of the abovementioned inert suspension media into the polymerization system.

          If the polymerization is carried out as a  
25           suspension or solution polymerization, use is made of an inert solvent customary for the Ziegler low-pressure process. For example, the polymerization is carried out in an aliphatic or cycloaliphatic hydrocarbon, for example propane, butane, hexane, heptane, isooctane,  
30           cyclohexane or methylcyclohexane. It is also possible to use a petroleum fraction or hydrogenated diesel oil fraction. Toluene can also be used. Preference is given to carrying out the polymerization in the liquid monomer.

35           Before addition of the catalyst, in particular the supported catalyst system (comprising the



metallocene prepared according to the invention and a supported cocatalyst), another aluminum alkyl compound such as trimethylaluminum, triethylaluminum, triisobutylaluminum, trioctylaluminum or isoprenylaluminum can be additionally introduced into the reactor to make the polymerization system inert (for example to remove catalyst poisons present in the olefin). This compound is added to the polymerization system in a concentration of from 100 to 0.01 mmol of Al per kg of reactor contents. Preference is given to triisobutylaluminum and triethylaluminum in a concentration of from 10 to 0.1 mmol of Al per kg of reactor contents. This makes it possible to select a small molar Al/M<sup>1</sup> ratio in the synthesis of a supported catalyst system. If inert solvents are used, the monomers are metered in in gaseous or liquid form.

The process of the invention makes it possible to prepare metallocenes in high yield using the adducts of the formula (I) and also enables new metallocenes to be obtained. The process of the invention also has a wide applicability so that a variety of structurally different types of metallocene can be synthesized, in particular bulky compounds.

The invention is illustrated by the following examples which do not, however, restrict the invention.

General procedures: Preparation and handling of the compounds were carried out with exclusion of air and moisture under argon (Schlenk technique). All solvents required were freed of water and oxygen before use by boiling for a number of hours over suitable desiccants and subsequent distillation under argon.

Example 1. Zirconium tetrachloride-(1,2-dimethoxyethane) adduct

A suspension of 18.5 g (80 mmol) of zirconium tetrachloride in 250 ml of dichloromethane is admixed at room temperature with 7.2 g (80 mmol) of 1,2-

dimethoxyethane and stirred at this temperature for 1 hour. The mixture is subsequently filtered and the filtrate is admixed at -30°C with 100 ml of pentane and stored at this temperature for 5 hours. The residue is  
5 filtered off, washed with pentane and dried under reduced pressure.

This gives 22 g (85%) of zirconium tetrachloride-(1,2-dimethoxyethane) adduct.

Example 1a. Hafnium tetrachloride-(1,2-dimethoxy-  
10 ethane) adduct

The corresponding hafnium tetrachloride-(1,2-dimethoxyethane) adduct is prepared using a method analogous to Example 1.

Example 1b. Zirconium tetrachloride-(1,2-S,S-  
15 dimethyl thioglycol) adduct

The corresponding zirconium tetrachloride-(1,2-S,S-dimethyl thioglycol) adduct is prepared by a method analogous to Example 1 using 1,2-S,S-dimethyl thioglycol.

20 Example 1c. Titanium tetrachloride-DME adduct

A solution of 19 g (100 mmol) of titanium tetrachloride in 250 ml of dichloromethane is admixed at 0°C with 9.0 g (100 mmol) of 1,2-dimethoxyethane and stirred at room temperature for another 1 hour. The  
25 solvent is subsequently taken off, giving 24 g (86%) of titanium tetrachloride-(1,2-dimethoxyethane) adduct as a yellow solid.

Example 2. Dimethylsilanediylbis(2-methyl-4-(2-methylphenyl)indenyl)zirconium dichloride

30 A solution of 1 g (2 mmol) of dimethylbis(2-methyl-4-(2-methylphenyl)indenyl)silane in 20 ml of toluene and 1 ml of THF is admixed with 1.5 ml (4 mmol) of a 2.66 molar solution of n-BuLi in toluene and the mixture is stirred for another 2 hours at 80°C. After  
35 deprotonation is complete, the mixture is allowed to cool to 40°C, 0.65 g (2 mmol) of zirconium

tetrachloride-(1,2-dimethoxyethane) adduct is added and the mixture is stirred for another 2 hours at this temperature. The solvent is then removed and the residue is extracted with 100 ml of dichloromethane.

5 Taking off the dichloromethane leaves the crude complex which is purified further by recrystallization from toluene. This gives 850 mg (65%) of the pure metallocene (rac/meso 1:1).

<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): 7.58-6.90 (m, 16H), 2.49-2.20  
10 (m, 12H), 1.51-1.27 (m, 6H).

Example 3. Dimethylsilanediylbis(2-methyl-4-(2,3-dimethylphenyl)indenyl)zirconium dichloride

The synthesis of dimethylsilanediylbis(2-methyl-4-(2,3-dimethylphenyl)indenyl)zirconium  
15 dichloride was carried out by a method similar to Example 2 using the zirconium tetrachloride-(1,2-dimethoxyethane) adduct and the complex was isolated in a yield of 61%.

<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): 7.58-6.8 (m, 14H), 2.48-2.22  
20 (m, 18H), 1.50-1.25 (m, 6H).

Example 4. Dimethylsilanediylbis(2-cyclohexyl-4-phenylindenyl)zirconium dichloride

The synthesis of dimethylsilanediylbis(2-cyclohexyl-4-phenylindenyl)zirconium dichloride was  
25 carried out by a method similar to Example 2 using the zirconium tetrachloride-1(1,2-dimethoxyethane) adduct. The complex was isolated in a yield of 59%.

<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): 7.65-7.06 (m, 16H), 6.92 (s, 2H), 2.88-2.75 (m, 2H), 2.00-0.95 (m, 20H), 1.49-1.28  
30 (m, 6H).

Example 4a. Dimethylsilanediylbis(2-cyclohexyl-4-phenylindenyl)zirconium dichloride

The synthesis of dimethylsilanediylbis(2-cyclohexyl-4-phenylindenyl)zirconium dichloride was  
35 carried out by a method similar to Example 2 using the analogous zirconium tetrachloride-(1,2-S,S-

dimethylthioglycol) adduct. The complex was isolated in a yield of 49%.

<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): 7.65-7.06 (m, 16H), 6.92 (s, 2H), 2.88-2.75 (m, 2H), 2.00-0.95 (m, 20H), 1.49-1.28 (m, 6H).

Comparative Example to Example 4. Dimethylsilanediylbis(2-cyclohexyl-4-phenylindenyl)zirconium dichloride

In a comparative experiment, the procedure of Example 4 was repeated using zirconium tetrachloride in place of the zirconium tetrachloride-(1,2-dimethoxyethane) adduct. In this case, no complex could be isolated.

Example 5. Dimethylsilanediylbis(2-cyclohexyl-4-phenylindenyl)hafnium dichloride

The synthesis of dimethylsilanediylbis(2-cyclohexyl-4-phenylindenyl)hafnium dichloride was carried out by a method similar to Example 2 using the analogous hafnium tetrachloride-(1,2-dimethoxyethane) adduct. The complex was isolated in a yield of 60%.

<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): 7.67-7.01 (m, 16H), 6.92 (s, 2H), 2.88-2.75 (m, 2H), 2.00-0.94 (m, 20H), 1.45-1.25 (m, 6H).

Example 6. Dimethylsilanediylbis(2-methyl-4-(2,4,6-trimethylphenyl)indenyl)zirconium dichloride

The synthesis of dimethylsilanediylbis(2-methyl-4-(2,4,6-trimethylphenyl)indenyl)zirconium dichloride was carried out by a method similar to Example 2 using the zirconium tetrachloride-(1,2-dimethoxyethane) adduct. The complex was isolated in a yield of 50%.

<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): 7.55-6.82 (m, 12H), 2.47-2.23 (m, 24H), 1.51-1.26 (m, 6H).

Example 7. Dimethylsilanediylbis(2,4-diphenylindenyl)zirconium dichloride

The synthesis of dimethylsilanediylbis(2,4-diphenylindenyl)zirconium dichloride was carried out by

a method similar to Example 2 using the zirconium tetrachloride-(1,2-dimethoxyethane) adduct. The complex was isolated in a yield of 57%.

<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): 7.81-6.91 (m, 26H, 6.75/6.69 (s, 2H), 1.45/0.41 (d, 6H, meso) 0.87 (s, 6H, rac).

Example 8. Dimethylsilanediylbis(2-isopropyl-4-phenylindenyl)zirconium dichloride

The synthesis of dimethylsilanediylbis(2-isopropyl-4-phenylindenyl)zirconium dichloride was carried out by a method similar to Example 2 using the zirconium tetrachloride-(1,2-dimethoxyethane) adduct. The complex was isolated in a yield of 51%.

<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): 7.70-7.03 (m, 18H), 3.20 (sept., 2H), 1.41 (s, 6H), 1.13 (m, 12H).

Example 9. Dimethylsilanediyl(tert-butylamido)(tetramethyl- $\eta^5$ -cyclopentadienyl)titanium dichloride.

The synthesis of dimethylsilanediyl(tert-butylamido)(tetramethyl- $\eta^5$ -cyclopentadienyl)titanium dichloride was carried out by a method similar to Example 2 using the titanium tetrachloride-(1,2-dimethoxyethane) adduct. The complex was isolated in a yield of 61%.

<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): 2.06 (s, 6H), 1.94 (s, 6H), 1.58 (s, 9H), 0.30 (s, 6H).

Example 9a. Dimethylsilanediyl(tert-butylamido)(tetramethyl- $\eta^5$ -cyclopentadienyl)titanium dichloride

A solution of 1 g (3.98 mmol) of dimethyl(tert-butylamido)(tetramethylcyclopentadienyl) silane in 45 ml of THF is admixed at 0°C with 2.98 ml (8 mmol) of n-butyllithium (2.68 molar in toluene) and the mixture is stirred for 1 hour at room temperature. This is subsequently added to a cooled (-78°C) solution of 1.15 g (3.98 mmol) of titanium trichloride-1,2-dimethoxyethane adduct (TiCl<sub>3</sub>\*1.5DME) in 45 ml of THF

and the resulting reaction mixture is slowly warmed to room temperature. After addition of 1.1 g (3.98 mmol) of lead(II) chloride, the suspension is stirred for another 12 hours. The solvent mixture is then removed under reduced pressure, the residue is taken up in dichloromethane and filtered through Celite. The filtrate is finally evaporated and admixed with pentane, as a result of which the product precipitates in the freezer. After removal of the mother liquor, 0.85 g (59%) of the complex is isolated.

Example 10. Dimethylsilanediylbis(2-methyl-4-phenylindenyl)titanium dichloride

The synthesis of dimethylsilanediylbis(2-methyl-4-phenylindenyl)titanium dichloride was carried out by a method similar to Example 2 using the titanium tetrachloride-(1,2-dimethoxyethane) adduct. The complex was isolated in a yield of 47%.

<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): 7.89-6.95 (m, 18H), 2.61/2.40 (s, 6H), 1.45 (d, 6H, meso), 1.41 (s, 6H, rac).

Example 11. [4-( $\eta^5$ -fluorenyl)-4-methyl-6-phenyl-( $\eta^5$ -4,5,6,7-tetrahydropentalenyl)]zirconium dichloride

4.7 ml (12.6 mmol) of n-butyllithium, 20% in toluene, are added dropwise at room temperature to 2.16 g (6 mmol) of 1-fluorenyl-3-phenyl-1-methyl-1,2,3-trihydropentalene in 50 ml of toluene. After stirring for 4 hours at 60°C, the mixture is cooled to 10°C. 1.94 g (6 mmol) of zirconium tetrachloride-(1,2-dimethoxyethane) adduct are added to the red suspension obtained in this way and the mixture is stirred for 3 hours at room temperature. After filtration through Celite, the filter is washed twice with 50 ml each time of hot (80°C) toluene. Evaporation of the combined filtrates to 10 ml, cooling to -30°C, filtration of the precipitated red powder and drying gives 0.970 g (1.9 mmol) of the complex (31%).

$^1\text{H}$ -NMR (300 MHz,  $\text{CDCl}_3$ ): 7.99-7.75, 7.52-6.93 (13 H, m, arom. protons), 6.32 (1 H, dd, arom. Cp-H), 6.16 (1 H, t, arom. Cp proton), 4.45 (1 H, dd,  $\text{CH}_2$ ), 4.17 (1 H, dd,  $\text{CH}_2$ ), 3.03 (1 H, dd, CH-Ph), 2.45 (3 H, s,  $\text{CH}_3$ ).

- 5 Example 12. Dimethylsilanediylbis(2,3,5-trimethylcyclopentadienyl) zirconium dichloride

A solution of 3 g (11 mmol) of dimethylsilanediylbis(2,3,5-trimethylcyclopentadienyl) silane in 20 ml of toluene and 1 ml of THF is admixed  
10 with 8.22 ml (22 mmol) of a 2.68 molar solution of n-BuLi in toluene and the mixture is stirred for 2 hours at 80°C. After cooling to 45°C, 3.91 g (12.1 mmol) of zirconium tetrachloride-(1,2-dimethoxyethane) adduct are added thereto and the mixture is stirred at 60°C  
15 for 2 hours. The solvent is removed and the residue is extracted with 125 ml of toluene. Taking off the toluene gives 2.85 g (60%) of the pure metallocene (pseudo-rac/pseudo-meso 1:1).

$^1\text{H}$ -NMR (300 MHz,  $\text{CDCl}_3$ ): 6.50 (s, 1H), 6.38 (s, 1H),  
20 2.25 (s, 3H), 2.20 (s, 3H), 2.16 (s, 3H), 2.12 (s, 3H), 1.98 (s, 3H), 1.88 (s, 3H), 0.98/0.94 (s, 6H), 0.95 (s, 6H).

## Claims:

1. A process for preparing a metallocene, which comprises reacting a ligand starting compound with an adduct of the formula (I),



where  $M^1$  is a metal of group III, IV, V or VI of the Periodic Table of the Elements or an element of the lanthanide or actinide series,

- 10 X are identical or different and are each halogen,  $C_1$ - $C_{10}$ -alkoxy,  $C_6$ - $C_{10}$ -aryloxy,  $C_1$ - $C_{10}$ -alkylsulfonate such as mesylate, triflate, nonaflate,  $C_6$ - $C_{10}$ -arylsulfonate such as tosylate, benzenesulfonate,  $C_1$ - $C_{10}$ -alkylcarboxylate such as acetate, formate, oxalate or 1,3-dicarbonylate  
15 such as acetylacetonate or fluorinated 1,3-dicarbonylate,

n is an integer and is 2,3,4,5 or 6 and corresponds to the oxidation number of the metal  $M^1$ ,

a is an integer or fraction and  $0 < a \leq 4$ ,

- 20 and D is a linear, cyclic or branched oligoether or polyether containing at least two oxygen atoms or an oligothioether or polythioether containing at least two sulfur atoms.

2. The process as claimed in Claim 1, wherein the  
25 ligand starting compound is deprotonated using a base.

3. The use of an adduct of the formula I as defined in Claim 1 for preparing a metallocene.



0732/970223

Abstract

Process for preparing metallocenes

The present invention relates to a process for preparing a metallocene, which comprises reacting a ligand starting compound with an adduct of the formula (I),



where  $M^1$  is a metal of group III, IV, V or VI of the Periodic Table of the Elements or an element of the lanthanide or actinide series, preferably titanium, zirconium or hafnium, particularly preferably zirconium,

X are identical or different and are each halogen,  $C_1$ - $C_{10}$ -alkoxy,  $C_6$ - $C_{10}$ -aryloxy,  $C_1$ - $C_{10}$ -alkylsulfonate such as mesylate, triflate, nonaflate,  $C_6$ - $C_{10}$ -arylsulfonate such as tosylate, benzenesulfonate,  $C_1$ - $C_{10}$ -alkylcarboxylate such as acetate, formate, oxalate or 1,3-dicarbonylate such as acetylacetonate or fluorinated 1,3-dicarbonylate, in particular chlorine, bromine, particularly preferably chlorine,

n is an integer and is 2,3,4,5 or 6 and corresponds to the oxidation number of the metal  $M^1$ ,

a is an integer or fraction and  $0 < a \leq 4$  and a is preferably in the range from 0.5 to 2.5 and is in particular 1, 1.5 or 2,

and D is a linear, cyclic or branched oligoether or polyether containing at least two oxygen atoms or an oligothioether or polythioether containing at least two sulfur atoms.

# Declaration, Power of Attorney

Page 1 of 3

0732/970223

We (I), the undersigned inventor(s), hereby declare(s) that:

My residence, post office address and citizenship are as stated below next to my name,

We (I) believe that we are (I am) the original, first, and joint (sole) inventor(s) of the subject matter which is claimed and for which a patent is sought on the invention entitled

Process for preparing metallocenes

the specification of which

☒ is attached hereto.

☐ was filed on \_\_\_\_\_ as

Application Serial No. \_\_\_\_\_

and amended on \_\_\_\_\_.

☒ was filed as PCT international application

Number PCT/EP 98/05588

on 03/09/1998

and was amended under PCT Article 19

on \_\_\_\_\_ (if applicable).

We (I) hereby state that we (I) have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

We (I) acknowledge the duty to disclose information known to be material to the patentability of this application as defined in Section 1.56 of Title 37 Code of Federal Regulations.

We (I) hereby claim foreign priority benefits under 35 U.S.C. § 119(a)–(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed. Prior Foreign Application(s)

Application No.	Country	Day/Month/Year	Priority Claimed
19739946.0	Germany	11 September 1997	<input checked="" type="checkbox"/> Yes <input type="checkbox"/> No

pnlskdec001 - 29

We (I) hereby claim the benefit under Title 35, United States Codes, § 119(e) of any United States provisional application(s) listed below.

\_\_\_\_\_  
(Application Number)

\_\_\_\_\_  
(Filing Date)

\_\_\_\_\_  
(Application Number)

\_\_\_\_\_  
(Filing Date)

We (I) hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s), or § 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. § 112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

**Application Serial No.**

**Filing Date**

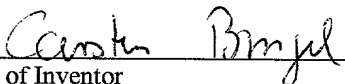
**Status (pending, patented,  
abandoned)**

_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____

And we (I) hereby appoint **Messrs. HERBERT B. KEIL**, Registration Number 18,967; and **RUSSEL E. WEINKAUF**, Registration Number 18,495; the address of both being Messrs. Keil & Weinkauff, 1101 Connecticut Ave., N.W., Washington, D.C. 20036 (telephone 202-659-0100), our attorneys, with full power of substitution and revocation, to prosecute this application, to make alterations and amendments therein, to sign the drawings, to receive the patent, and to transact all business in the Patent Office connected therewith.

We (I) declare that all statements made herein of our (my) own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Carsten Bingel  
NAME OF INVENTOR

  
Signature of Inventor

Date

03/02/2000

Elsa-Brandström-Str. 13-15

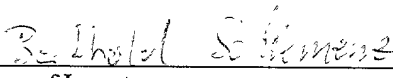
65830 Kriftel

Germany

Citizen of: Germany

Post Office Address: same as residence

Berthold Schiemenz  
NAME OF INVENTOR

  
Signature of Inventor

Date

03/02/2000

Loreleistrasse 40

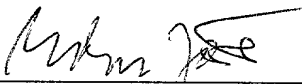
65929 Frankfurt

Germany

Citizen of: Germany

Post Office Address: same as residence

Markus Göres  
NAME OF INVENTOR

  
Signature of Inventor

Date

03/02/2000

Im Bubenhain 3

65760 Eschborn

Germany

Citizen of: Germany

Post Office Address: same as residence